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PATENT SPECIFICATION.

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(Under Section 91, sub-sections (2) and (4) of the Patents and Designs Acts, 1907 to 1939, a single Complete Specification was left in respect of this Application and of Application No. 2733/40 and was laid open to inspection on Aug. 19, 1940).

COMPLETE SPECIFICATION.

Improvements in or relating to the Conversion of Hydrocarbon Oils in the presence of Powdered Contact Materials.

We, STANDARD OIL DEVELOPMENT COMPANY, a corporation duly organized and existing under the laws of the State of Delaware, United States of America, having an office at Linden, New Jersey, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention is directed to the conversion of hydrocarbon oils and pertains more particularly to a process of and apparatus for processing crude petroleum oil to produce as a primary product, motor fuel having a high octane rating.

The invention in its entirety comprehends the processing of crude petroleum oils in which the crude oil is initially segregated into separate fractions and the separate fractions so segregated then separately treated under selective conditions for the conversion, of such fractions into motor fuel products of high anti-knock value. The invention is concerned primarily with the treatment of said selective fractions in the presence of a pulverized contact material which in the case of the lighter fractions, such as naphtha or gas oils, preferably has catalytic action whereas the pulverized material employed in the treatment of the heavier residual stocks may or may not have catalytic activity.

It has heretofore been proposed to crack hydrocarbon oil in the presence of a solid contact mass having catalytic activity, such as, for example, naturally active or activated clays and certain synthetic compounds of similar adsorbent nature.

According to one of the better known methods of carrying out the catalytic process, the oil in vapor form preheated to the desired cracking temperature is passed through a reaction zone containing a solid mass of contact material. The

rate of flow of the oil vapors is controlled to obtain the desired conversion into lower boiling distillate products and the reaction products are then passed into a conventional fractionating equipment for the separation of desired motor fuel products from the unconverted oil.

During the cracking operation, the catalytic material gradually becomes fouled with carbonaceous deposits which reduces the activity of the catalyst until eventually a point is reached where it becomes necessary to regenerate the catalyst to restore its activity. When operating according to the method above described, the cracking operation is continued for a predetermined period until the activity of the catalyst is dropped to a point where it becomes no longer capable of effecting the desired conversion. The cracking cycle is then interrupted, the catalyst purged of residual oil and carbonaceous deposits are burned from the catalyst by passing an oxidizing gas through the catalyst. After completing the regeneration of the catalyst, the mass is then purged of regenerating gases and subjected to another cracking cycle. When operating in this manner, it has also been proposed to mold the catalyst into small cylinders, discs, pills or other shapes of uniform size to insure more uniform distribution of the oil vapors through the mass and reduce the resistance of the contact mass to the flow of gases and vapors therethrough.

This method of operating has a number of objections. First, because of the necessity of frequently interrupting the cracking cycle to effect regeneration of the catalyst, it is necessary to provide a number of reaction chambers in order to operate the process continuously, so that one chamber may be undergoing the cracking cycle while others are undergoing regeneration. The original investment, therefore, necessary for providing an apparatus capable for operating at

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commercial capacities becomes relatively large. Secondly, since the conditions for carrying out the cracking cycle and for carrying out regeneration are widely different, a design capable of most effectively carrying out the cracking cycle is not particularly adapted for effecting rapid regeneration of the catalyst mass. On the other hand, if the reaction chamber is designed so as to obtain rapid regeneration of the catalyst mass, it may not be particularly suitable for carrying out the catalytic cracking operation.

The present invention comprises a process for obtaining motor fuel of high antiknock value from a crude petroleum oil wherein the crude oil is first separated into a plurality of fractions of different boiling ranges which fractions are separately vaporized and mixed with pulverulent solid contact materials to form suspensions of the said solid materials in the said vapors and the said suspensions are passed through separate reaction zones and maintained therein for such time and under such conditions as to convert the oil fractions into motor fuels of high antiknock value which are then separated from the reaction products.

In accordance with the invention the crude oil is conveniently fractionated into a light fraction comprising principally gasoline constituents which is treated with a reforming catalyst capable of converting the fraction into gasolines of high antiknock value, an intermediate fraction comprising principally constituents boiling within the gas oil range which is treated with a cracking catalyst capable of cracking the fraction to produce motor fuels of high antiknock value, and a heavy fraction comprising heavy residual oils boiling above the gas oil range and which is treated with a contact material to break the viscosity of the fraction and produce products of lower boiling ranges which can be further treated together with the lighter fractions.

According to further features of the invention, each fraction is vaporized and mixed in the form of a restricted stream with the powdered catalyst preferably in the form of a suspension in an inert gas and the mixture thus obtained is passed in a restricted stream through a reaction zone suitably in the form of an elongated restricted passage way at a velocity sufficient to return the powdered catalyst in suspension in the gas mixture.

Other features of the invention will be readily apparent from the following description of the process and the accompanying drawings illustrating one convenient method and apparatus for carrying the invention into effect, Fig. 1 is a

diagrammatic illustration of an apparatus adapted for processing crude petroleum stock; Fig. 1-A is a continuation of Fig. 1 on lines 1—A—1A; Fig. 2 is a diagrammatic illustration of an apparatus suitable for regenerating the catalytic mass employed in the treatment of such oils, and Fig. 3 is a sectional view of an apparatus adapted for preconditioning the powdered catalytic material for injection into the oil stream.

Referring to Fig. 1, the oil to be processed, which is preferably a crude petroleum product is introduced into the apparatus through charge line 10, provided with pump 11 which forces the oil through a preheating coil 12 located in furnace 13. The oil during its passage through the heating coil 12 is preferably heated to incipient cracking temperature sufficient to vaporize all constituents vaporizable without decomposition. The outlet temperature of the oil after passing through the heating coil 12 and preheated to vaporize the major constituents thereof is transferred through transfer line 14 to a crude distilling and fractionating tower 15. The crude fractionating tower 15 is provided with suitable fractionating elements, such as discs and annular rings, baffles, bubble trays, Raschig rings or the like for fractionating vapors liberated in the bottom section of the tower. The tower 15 is preferably provided with a trap-out tray 16 for collecting condensate formed in the intermediate section of the tower 15. This condensate is preferably a gas oil fraction having an initial boiling point between 400 and 500° F. and a final boiling point between 650 and 750° F. Products collected in the bottom section of the tower 15 comprising unvaporized residue and vapors condensed below the trap-out tray 16 are withdrawn from the tower 15 through line 17 and treated as hereinafter described. Condensate collected on trap-out tray 16 is withdrawn through line 18 and further processed as later described.

Vapors remaining uncondensed in the fractionating tower 15 and which may or may not contain all or part of the gasoline constituents liberated from the crude petroleum pass overhead through line 19 to a condenser 20 wherein the light normally liquid constituents are condensed. Products from the condenser 20 pass to a receiver 21 wherein the liquids condensed in the condenser 20 separate from the uncondensed constituents. Uncondensed normally gaseous constituents in the fractionating tower 15 are removed from receiver 21 through line 22. Liquid distillate collected in the receiver 21 is withdrawn therefrom through line 23 and may

be removed from the system through line 24, or it may be passed through line 25 and 26 and subjected to catalytic treatment as later described. If desired, a portion of such distillate may be returned to the top of the fractionator 15 as reflux therefor.

According to one phase of the invention, the fractionating tower 15 is provided with a second trap-out tray 27 having a draw-off line 28, and the top temperature thereof is controlled to condense a naphtha fraction for further treatment to improve the octane number thereof. This naphtha fraction may comprise the total gasoline fraction of the crude charge, but preferably comprises a heavy naphtha fraction having an initial boiling point between 200—250° F. and a final boiling point between 400—500° F. The straight run heavy naphtha fraction collected on the trap-out tray 27 is withdrawn through line 28 and passed to a heating coil 29 located in furnace 30. The oil during its passage through the heating coil 29 is vaporised and preferably heated to the desired reforming temperature, such as from 700—1000° F., to improve the octane number thereof. The naphtha, after passing through the pre-heating coil 29 passes through transfer line 31 to an injector 32 wherein it is injected into a stream of powdered catalyst.

It has been found that in order to avoid plugging of the catalyst feeding mechanism due to formation of coke therein and to obtain more intimate dispersion of catalyst and oil vapors, it is desirable to inject into the powdered catalyst a heat stable gaseous stream, such as steam, nitrogen, or low molecular weight hydrocarbon gases, for example, methane and ethane, before contacting the catalyst with the oil vapors. The gas so introduced into the catalyst, forms a gaseous shield between the feeding mechanism and the oil vapors and thus prevents the oil vapors from contacting the feeding mechanism. Fig. 3 is a cross section of an apparatus for mixing the powdered catalytic material with the oil vapors.

Referring to Fig. 3, the numeral 33 designates a hopper containing the powdered catalyst 34. The bottom of the hopper 33 is provided with a screw conveyor 35 which feeds the catalyst from the hopper 33 through conduit 36 into a chest or chamber 37. The conveyor 35 is preferably provided with a compression screw having the spaces between the flights of progressively decreasing size toward the outlet. Extending through the wall of chamber 37 and preferably opposite the end of the screw conveyor 35

is a nozzle 38 through which is introduced an inert gas, such as steam, nitrogen, hydrogen, light hydrocarbon gases or the like. This stream of inert gases impinges upon the product issuing from the conveyor 35 and breaks up lumps which may be formed by passing through the conveyor 35. A heavy dense dispersion of powdered material and inert gas forms within the chamber 37 and is passed through a nozzle 39 and conduit 40 to the injection chamber 32.

The oil vapors introduced into the injection chamber 32 are intimately dispersed within the powdered material and the suspension or dispersion of oil vapors, inert gas and powdered material is passed from the injection chamber 32 through line 41. (See Fig. 1).

Returning now to Fig. 1: the pulverized catalyst introduced into the injector 32 may be any suitable reforming catalyst such as active or activated clays, mixed oxides of silica and alumina, bauxite or the mixed oxides of the third and sixth groups of the Periodic system. A particularly desirable catalyst is a co-precipitated mixture of chromium oxide and aluminium oxide. The catalyst employed is preferably a finely-divided pulverized material having a particle size ranging, for example, between 200 and 400 standard mesh.

The oil vapors and inert gases with the powdered catalyst dispersed therein pass from the injection chamber 32 through a line 41 to a reaction zone 42. For illustrative purposes, the reaction zone 42 has been shown in the form of a heating coil disposed within the furnace setting 43. The reaction zone may, however, be of any desired construction providing an elongated restricted passageway, so that the velocity of the vapors passing through the reaction zone is sufficient to maintain the powdered catalyst in suspension therein. For example, in lieu of a heated coil such as shown, an unheated tubular coil or a heated or unheated reaction chamber provided with suitable baffles to maintain the gases at sufficient velocity to hold the catalyst in suspension may be employed.

The relative proportion of catalyst and oil vapors, temperature, pressure and time of contact within the reaction zone will depend upon the nature of the naphtha to be treated, the amount of octane improvement desired and other factors, so that it is impossible to specify a specific condition of operation which will be suitable for all cases. For obtaining an anti-knock improvement of from 5—15 octane number on the virgin heavy naphtha having a boiling range of from 130

250—500° F. from an East Texas crude oil, the relative proportion of catalyst and oil vapors may be of the order of .5 to 3 lbs. of catalyst per pound of naphtha
5 treated, the temperature between 900—1000° F., and the time of contact may be from 10 to 80 seconds. This process is preferably operated at substantially atmospheric pressure, but sub-atmospheric or
10 mild super-atmospheric pressure, such as from 2 to 20 atmospheres may be employed.

The products from the reaction zone 42, after having undergone the desired reforming treatment therein, are transferred through line 44 to a suitable separator for removal of solid from gases, such as a cyclone separator 45, (see Fig. 1—A for separation of the powdered catalyst therefrom. The powdered catalyst separated in the separator 45 passes downwardly through a baffle tower 46 preferably located directly below the separator, countercurrent to a stream of inert gas such as steam, introduced in the bottom section of the tower. The inert gas stream serves to strip the separated catalyst of residual oil constituents remaining on the catalyst. The separated catalyst after passing through the baffle tower 46 is collected in a catalyst receiver 47 from whence it is passed through a suitable pressure sealed conveyor, such as a star conveyor 48 to a regenerating circuit later described.

The oil vapors and gases after having been freed of at least the bulk of the catalyst material in the cyclone separator 45 are removed therefrom through line 49 and may be passed to conventional fractionating equipment for the fractionation of the oil vapors therein. However, according to a more specific phase of the invention and particularly when steam is employed as an inert gas for dispersing the catalyst into the oil vapor and for stripping the separated catalyst of residual oil vapors, it is preferred to separate the steam from the oils before fractionation.

To this end, the gases removed from the separator 45 through line 49 are passed to a condenser 51 wherein normally liquid products including steam are condensed. Products from the condenser 51 then pass to a gas separator 52 wherein normally gaseous constituents separate from the liquid. The normally gaseous constituents pass from the separator 52 through line 53 and may be sent to a suitable adsorption system for the recovery of gasoline constituents therefrom.

Liquid separated in the separator 52 is withdrawn therefrom through line 54 and passed to a water separator 55 wherein

the water and oil phases are allowed to stratify. The water is removed from the water separator 55 through line 56 and the oil is passed through line 57 to a combined distilling and fractionating tower 70 58 for distilling and fractionating the products so separated. If desired, a heat exchanger 59 may be placed in the line 57 leading from the water separator 55 to the distilling and fractionating tower 75 58 to preheat the oil prior to introduction into the fractionating tower.

Any powdered catalyst not separated in the separator 45 will accumulate in the water phase of the water separator 55 and be withdrawn through line 56. It is preferred to effect substantially complete removal of the powdered catalyst while the oil products are in vapor form, so that the water withdrawn through line 56 will 80 be substantially free of catalyst and can be discarded. If one cyclone separator is not sufficient to effect substantially complete removal of the powdered catalyst from the oil vapors, additional separators 85 may be inter-connected in series with the separator 45.

It is within the purview of this invention, however, to remove only the bulk of the catalyst material in the cyclone 95 separator 45 in relatively dry form and to separate the remainder of the powdered catalyst in the form of a water catalyst slurry in the water separator 55. In the latter case, the water removed through 100 line 56 containing powdered catalyst may be sent to a filtering device (not shown) of any suitable construction for separation of the powdered catalyst therefrom. The residue from the filtering operation 105 may be then dried and subjected to regeneration and returned to the process.

The distillate introduced into the distilling and fractionating tower 58 is subjected to distillation and fractionation 110 therein to separate a desired motor fuel distillate from remaining higher and lower boiling constituents. Higher boiling distillate undesired in the final motor fuel product may be collected in the 115 bottom of the fractionating tower 58 and may be withdrawn therefrom through line 60 and subjected to further treatment as hereinafter described. The motor fuel constituents in vapor form are removed 120 from the fractionating tower 58 through line 61 to a condenser 62 wherein the motor fuel distillate is condensed. The products from the condenser 62 pass to a distillate receiver 63 wherein the distillate separates from any gases liberated during the distillation thereof. The liquid distillate collected in the receiver 63 is withdrawn through line 64 and may be subjected to any further finishing treat- 130

ment desired. Gases separated in the receiver 63 are removed overhead through line 65 and may be sent to a suitable adsorption system for recovery of gasoline constituents therefrom.

According to one phase of this invention, a part or all of the gases separated in the receiver 63 is recycled to the reaction zone through lines 66, 67, blower 10 68, and lines 69 and 70 (see Fig. 1) to the inlet side of the reaction coil. These gases will normally contain a relatively high percentage of hydrogen, which will serve to reduce the amount of coke formed 15 on the catalyst, during the process, and other constituents which may be polymerized or reacted with the oil to improve the gasoline yield. When operating in this manner, it is preferred also to recycle 20 the gases removed from the initial gas separator 52 through line 53. These gases may be passed through lines 53 and 71 to recycle line 66 and there combined with recycle gases from receiver 63, or, if 25 desired, gases from separator 52 may be introduced into the fractionating tower 58 through line 72 to assist the distillation and fractionation therein. If desired, additional hydrogen may be added to the 30 recycle gas through line 67.

In lieu of carrying out reforming of heavy naphtha or total naphtha fraction within the reaction zone 42, the invention also contemplates the combined reforming 35 and condensation of light naphtha or total overhead products from the crude fractionating tower 15, to form higher molecular weight hydrocarbons as well as to improve octane number. To this end, the 40 heavy naphtha withdrawn from trap-out tray 27 through line 28 may be removed from the system through line 28¹ and the overhead vapor fraction from the fractionating tower 15 passed directly 45 through lines 19, 19¹ and 26 to the inlet side of the heating coil 29 or the light naphtha fraction collected in receiver 21 may be passed through lines 23, 25 and 50 26 to the inlet side of the heating coil 29. When processing this type of stock, the temperature, time of contact and nature 55 of the catalyst employed, will be regulated to accomplish condensation or polymerization of low molecular weight hydrocarbons into higher boiling products. Any suitable polymerizing or condensing catalysts, such as activated clays, aluminium chloride or complex salts of aluminium chloride, for example, 60 sodium aluminium chloride, may be employed alone or supported on a suitable carrier. The temperatures for carrying out this type of reaction may be the same or somewhat lower than that employed for reforming, such as from 400—1000° F. 65

Returning to the crude fractionating tower 15 (see Fig. 1) the gas oil fraction collected in the trap-out tray 16 and removed through line 18 is forced by means of pump 75 through a preheating 70 and vaporizing coil 76 located in furnace 77. The oil during its passage through the heating coil 76 is vaporized and preferably heated to the desired reaction temperature for carrying out catalytic cracking treatment. This temperature, may for example, be of the order of from 750—900° F. 75

The oil after passing through the heating coil 76 is passed through line 78 to a separator 79 wherein any unvaporized constituents entrained in the oil passing through the preheating coil are separated. Liquids separated in the separator 79 are withdrawn through line 80 and may be rejected from the system and may be treated as hereinafter described. Vapors from the separator 79 pass overhead through line 81 to an injector 82 wherein they are dispersed in a suspension of powdered catalyst and inert gas. The method of an apparatus for injecting the powdered catalyst into the gas oil vapor stream is the same as that employed for injecting powdered catalyst into the 95 naphtha stream hereinbefore described. For more complete details, therefore, reference is made to the preceding description. 90

In case the gas oil charged to the pre-heating coil 76 is relatively free of unvaporizable constituents, the separator 79 may be omitted or the oil vapor may be by-passed around the separator through line 83. 100

The dispersion of oil vapours and catalyst from the injection chamber 82 passes through line 84 to a reaction coil 85 located in the furnace 86. 105

The catalyst employed for the cracking of the gas oil may be any suitable cracking catalyst, such as for example, active or activated clays or synthetic gels consisting principally of silica and alumina. The catalyst is preferably in finely pulverized condition, having a particle size, for example, ranging between 200—500 standard mesh. 110

The relative proportions of catalyst and oil vapors employed, the temperature, velocity and time of contact may vary over a substantial range depending upon the nature of the gas oil cracked, the amount of conversion desired and other factors. 115

For example, when cracking a virgin East Texas gas oil having an A.P.I. gravity of from 30 to 40 employing activated clay known as Superfiltrol, the relative proportions of catalyst and oil 120

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vapors are preferably between the range of .5 parts to .3 parts of catalyst per part of oil by weight and particularly between one and two parts of catalyst per part of oil. The temperature may range between 800 and 1000°, preferably between 875 and 925° F. The pressure employed may be atmospheric or a mild super-atmospheric pressure, such as from 2 to 20 atmospheres. The time of contact of the oil vapors within the reaction zone in such case is preferably from 10 to 90 seconds. The velocity of the oil vapors catalyst suspension passing through the reaction zone should be sufficient to maintain the powdered catalyst dispersed within the vapors.

The oil vapors and catalyst after being maintained within the reaction coil 85 for a period sufficient to obtain the desired conversion thereof, is passed through transfer line 87 to a separator 88 (see Fig. 1—A) wherein the powdered material is separated from the cracked products. This separator may be the conventional cyclone separator, such as previously described, or any other type of separator capable of removing solids from gases. The catalyst separated in the cyclone separator 88 is charged into the top of a vertical baffle tower 89 and passes downwardly therethrough in countercurrent contact with an inert gaseous medium, such as steam introduced at 90. The inert gaseous medium tends to strip the separated catalyst of residual oil vapors remaining absorbed thereon. The stripped catalyst from the vertical tower 89 is discharged into a catalyst receiver 91. Separated catalyst collected in the receiver 91 is removed therefrom by means of suitable pressure type feeding mechanism, such as a rotary star conveyor 92 and is passed to suitable regenerating equipment hereinafter described.

Gases separated in the cyclone separator 88 comprising the cracked oil products together with inert constituents introduced as a dispersing medium for the catalyst and for purging the separated catalyst in the tower 89 pass from the cyclone separator through line 93 and may be passed directly to suitable fractionating equipment for the separation of the desired motor fuel products therefrom. It is preferable, however, when steam is used as a diluent, to cool the product so as to condense the steam before subjecting the product to fractionation. To this end, as shown on the drawing, the products from the line 93 pass to a condenser 94 wherein the products are cooled to a temperature below the boiling point of water so as to condense steam contained therein. Products from the condenser 94 pass to a gas separator 95 wherein normally gaseous constituents formed in the process are separated from the liquid condensed in the condenser 94. Gases separated in the gas separator 95 are passed overhead through line 96 having a valve for imposing the desired back pressure on the system. These gases may be passed to a suitable absorption equipment for the recovery of gasoline constituents therefrom or may be recycled directly to the cracking zone as later described.

Liquid collected in the gas separator 95 comprising the oil products together with condensed steam is removed therefrom through line 97 and passed to a water separator 98 wherein the water and oil phases are allowed to stratify. The water is withdrawn through line 99 and the oil fraction passed through line 101 and pump 102 to a fractionating column 103 wherein the oil products are subjected to a combined distilling and fractionating process. If desired, the oil prior to being introduced into the fractionating column 103 may be preheated by passing through a suitable heat exchanger 104.

The temperature of the combined distilling and fractionating tower 103 may be controlled to vaporize and fractionate only the lower boiling motor fuel distillate without vaporizing any substantial amount of the higher boiling condensate fraction, or the temperature may be such as to vaporize the total oil fraction so as to permit segregation of such fraction into a plurality of individual cuts for further treating as hereinafter described. The total higher boiling fraction boiling above the desired motor fuel products may be withdrawn from the fractionating tower 103 through line 106 and a portion thereof passed through lines 107, 108 and heat exchanger 109 back to the bottom of the tower to supply the necessary heat for effecting the distillation. Liquid collected in the bottom of the tower 103 and not recycled through a suitable heat exchanger may be withdrawn from the system through line 111 or passed through lines 112 or 113 for further processing as later described.

As before mentioned, the liquid products collected in the bottom of the fractionating tower 103 may comprise the total higher boiling constituents of the oil boiling above the motor fuel products. However, in some cases, it may be desirable to separate the heavy condensate into separate fractions. To this end, the fractionating tower 103 may be provided with trap-out trays for separately collecting individual fractions of such condensate. For example, a trap-out tray 114 may be provided adjacent the bottom of the tower 103.

so that the liquid collected in the bottom of the tower comprises, for example, from 5-10% of the total condensate formed in the tower. The product collected in the trap-out tray 114, comprising, for example, a heavy gas oil fraction boiling between the ranges of 550 to 750° F. may be withdrawn from the trap-out tray 114 through line 115 and subjected to further processing as later described.

Also, the tower 103 may be provided with a second trap-out tray 117 positioned in the upper section of the tower for separately collecting a light gas oil fraction which may be withdrawn from a trap-out tray 117 through line 118 and rejected from the system or subjected to further treatment as later described.

Vapors remaining uncondensed or separately vaporized in the fractionating tower 103 pass overhead therefrom through line 119 into a condenser 120 wherein the desired motor fuel products are condensed. Products from the condenser 120 may pass to a receiver 121 wherein any normally gaseous constituents liberated during the distillation and fractionation within the fractionating tower 103 may be separately removed through line 122 having a valve for imposing the desired back pressure on the fractionating tower. These gases may be passed to a suitable absorption system for the recovery of gasoline constituents therefrom. Motor fuel distillate collected in receiver 121 may be withdrawn through line 123 and subjected to any further finishing desired for the production of the final marketable product. This product may be blended with the reformed product collected in receiver 63 and if desired, a portion thereof may be returned to the top of the fractionating tower 103 as reflux therefor. Gases separated in receiver 121 and withdrawn through line 122 may be rejected from the system through line 124 or may be passed through line 125 to recycle line 66 and returned to the process. If desired, a portion of the recycle gas may be passed through lines 66, 67, blower 68, lines 69, 126 and 127 to the inlet side of the reaction coil 85.

As previously described in connection with the reforming process, it is preferred to remove substantially completely all of the powdered catalyst within the separator 88 prior to passing the vapors to the condenser 94. If the single cyclone separator 88 is ineffective to remove completely the powdered catalyst from the oil vapors, additional separators may be interconnected in the vapor line 93 for effecting further removal.

The invention further contemplates,

however, the removal of the bulk of the catalyst powdered material by means of the separator 88 while the reaction products are in vapor form and then removing the remainder by filtering the water phase separated in the water separator 98. The water withdrawn through line 99, for example, may be passed to a suitable filter for the separation of any powdered catalyst contained therein and the filtered residue dried and subjected to regeneration before returning to the operation.

Returning again to the crude fractionating tower 15 (see Fig. 1) the bottoms withdrawn therefrom through line 17 are forced by means of pump 130 to a viscosity breaking unit wherein these products are converted into vapors and coke. Bottoms from the tower 15 are forced by means of pump 130 through line 131 to a preheating coil 132, located in furnace 133. The oil during its passage through the heating coil 132 is preferably heated to the maximum temperature permissible without involving coking difficulties. If desired, steam may be introduced through line 134 to assist in vaporization and further treatment of the oil as later described.

In lieu of steam, residual gases formed in the processes and separated in receivers 63 and 121 may be passed through lines 67 and 126 and introduced into the heavy oil stream at the inlet side of the heating coil 132. A portion of such residual gases may also be passed through line 126¹ and introduced into either or both of the heating coils 29 and 76. As previously mentioned, a part or all of the residual gases may be injected directly into the dry catalyst before contacting the same with the oil vapors. The outlet temperature of the oil from the heating coil 132 may, for example, be of the order of from 800-900° F.

Products from the heating coil 132 pass through line 135 to an injection chamber 136 wherein they are injected into a stream of powdered material suspended in a stream of inert gas. If desired, a portion or all of the oil from the bottom of the chamber 15 may be bypassed around the furnace 132 through line 137 and passed directly into the injection chamber 136. The method of and apparatus employed is the same as that described for suspending the catalyst into the stream of naphtha vapors for carrying out the reforming operation earlier described. The suspension or dispersion of oil and powdered material formed in the injection chamber 136 passes through line 138 to a reaction coil 139 preferably located in the furnace 140. 130

The pulverized material introduced into the oil in injection chamber 136 may be an active cracking catalyst but is preferably a relatively inactive cracking catalyst or an inert material such as pumice, kieselguhr, spent clay or any other type of solid adsorbent material. In this case, the powdered material is intended to serve primarily as a carrier for the coke formed during the viscosity breaking operation.

The relative proportions of powdered material and oil, the temperature and length of treatment within the reaction coil 139 in this case is regulated to convert the oil into vapors and coke within the reaction zone.

The primary objective of the reaction within coil 139 is to reduce the viscosity of the heavy oil and convert it into a gas oil suitable for catalytic cracking along with the virgin gas oil from the crude fractionator rather than to convert said heavy oil directly into gasoline. The conditions within the reaction coil are controlled to attain this objective. It will be understood, of course, that minor amounts of gasoline are normally formed in carrying out the viscosity breaking treatment but this is incidental.

The products from the reaction coil 139 pass through line 141 to a cyclone separator 142 or other suitable apparatus for separating the powdered material from the cracked products. Powdered material separated in the separator 142 is passed to a vertical tower 143 containing suitable baffles for effecting intimate contact between the separated material and an inert gaseous stream passing countercurrently therethrough. The inert gaseous stream may be steam introduced through line 144. The powdered material after being stripped of volatile residual oil during its passage through the tower 143 is charged into a catalyst receiver 145 having a conveyor 146 for transferring the material to the suitable regenerating unit later described.

Cracked or viscosity broken products separated in the separator 142 are withdrawn through line 147. Products from the line 147 are preferably passed through lines 147 and 148 and combined with the virgin gas oil from the crude fractionator 15 on the inlet side of the preheating coil 76 or through lines 147 and 149 to the outlet side of the coil 76, and cracked with the virgin gas oil as previously described. It may be desirable in some cases, to subject the products from the separator 142 to fractionation to segregate a gas oil fraction therefrom. To this end, the products from line 147 may be passed through line 150 and combined with over-

head products from separator 88 for further fractionation therewith.

As a second alternative, the overhead from the separator 142 may be subjected to separate condensation to remove the final traces of powdered material therefrom before combining the oil products with the virgin gas oil. To this end, the products from the separator 142 may be passed through lines 147, 150, 151 to a separate condenser 152 wherein normally liquid products are condensed.

Products from the condenser 152 pass to a gas separator 153 wherein any normally gaseous products formed in the viscosity breaking process are separated. The gases so separated are removed from the separator 153 through line 154 having a valve which may be operated to impose the desired back pressure on the process. Liquid collected in the gas separator 154 passes through line 155 to a water separator 156 wherein the water and oil phases are allowed to stratify. The water may be withdrawn through line 157. The oil phase is withdrawn from the water separator 156 through line 158 which merges with line 148 leading to the inlet side of the preheating coil 76 where it combined with the virgin gas oil withdrawn from the trap-out tray 16 of the crude fractionating tower 15.

The separate condensation of the products from the separator 142 is of particular advantage in cases where a final portion of the powdered material is separated out in the form of a slurry in the water separator 152. As previously described, the invention contemplates two methods of separating the powdered material from the cracked products. In the one case, the total powdered material is separated in a relatively dry state from the oil vapors prior to condensation. In the second case, the bulk of the powdered material is separated out in the dry state and the final portion is separated by a wet method, or in other words, by the condensation of the cracked products and the steam to form a water slurry which may be later filtered and regenerated.

In case a trap-out tray 114 is provided in the fractionating tower 103 so as to segregate a high boiling fraction in the bottom of the tower, the higher-boiling fraction may be passed through lines 112 to the inlet side of the preheating coil 132 and combined with the residual fraction from the crude separator 15. Also, tar from the tar separator 79 may be passed to the inlet side of the preheating furnace 132 processing crude residual stock by merging line 80 with line 112 as shown. Cycle stock collected in trap-out tray 114 and withdrawn therefrom through line 130

- 115 or the total cycle from the bottom of the fractionating tower 103 may be recycled through line 116 to the inlet side of the heating coil 76 and combined with 5 crude gas oil from the crude fractionator 15. Bottoms from the fractionating tower 58 may also be recycled by merging line 60 with line 116.
- A part or all of the light cycle stock 10 collected in trap-out tray 117 and withdrawn through line 118 may be passed through line 159 to line 112 and employed for reducing the viscosity of the oil passing through the preheating coil 132 and 15 to assist in vaporizing the oil.
- The catalyst or powdered material separated from the reaction products in the three operations above described is preferably regenerated to remove carbonaceous deposits contained thereon as a 20 result of the treatment and returned to the catalyst hoppers for further use. Figure 2 illustrates an apparatus suitable for effecting the regeneration of the 25 powdered material. Referring to Fig. 2, the numeral 160 designates a receiver for catalysts separated from the reaction products and corresponds to receivers 47, 91 and 145 of Fig. 1. The catalyst collected 30 in the receiver 160 is transferred by means of suitable conveyor mechanism capable of maintaining a pressure seal, such as, for example, a star conveyor 161, and is injected into a stream of hot regenerating 35 gases passing through line 162. The regenerating gases are heated to a temperature sufficient to ignite the carbonaceous deposits contained on the catalyst. The regenerating gas containing the powdered catalyst passes from line 162 through a regenerating zone 163. This regenerating zone may be in the form of a tubular coil located within a waste heat boiler 164 for the recovery of heat 40 liberated during the regenerating process. Air or other oxidizing gas capable of supporting combustion within the regenerating zone is introduced through line 165 and is forced by means of blower 45 166 to any one or more of a number of different points in the regenerating circuit. For example, a part or all of the air necessary to regenerate the catalyst 50 may be introduced into the regenerating stream before introduction of the powdered material therein, or it may be introduced at spaced points in the regenerating zone.
- After completion of the regeneration in 55 the regenerating zone, the regenerated products pass through line 167 to a separator 168 for the separation of the regenerated powder from the regenerating gases. The powder separated in the separator 168 is charged downwardly

through a vertical tower 169 containing suitable baffles for effecting intimate contact between the regenerated catalyst and the inert gaseous medium passing upwardly through the tower counter-current to said powdered material. This inert medium is introduced into the bottom section of the tower and serves to strip the regenerated catalyst of regenerating gases absorbed thereon. The regenerated powdered material, after being stripped of residual regenerating gases in the tower 169 is passed into a catalyst receiver 170 from whence it is transferred by suitable conveyor mechanism into the various catalyst hoppers in the reforming, cracking and viscosity breaking circuit. In order to make unnecessary mechanical means for transfer of the regenerated catalyst into the hopper, the separators 168 and stripping tower 169 may be super-imposed upon each of the catalyst hoppers shown in Fig. 1. When the same type of catalyst is employed in the reforming, cracking and viscosity breaking operation, one regenerating circuit may be employed for regenerating all of the catalysts from the three operations. When different catalysts are employed for the three operations, a separate 80 regenerating unit for each circuit should be provided.

The regenerating gases separated in the separator 168 of the regenerating circuit (see Fig. 2) are removed from the separators through line 172 and may be rejected from the system through line 173. It is preferred, however, to recycle a portion of the gases so separated to the regenerating zone as a diluent for the air employed for burning the carbonaceous 100 deposits. For example, a part of the gases separated in the separator 168 may be passed through lines 172, 174, heat exchanger 175, lines 176, 177 and blower 110 105 178 to the line 162. In event it is desired to use a diluent other than spent regenerating gases for controlling the regenerating temperature within the regenerating zone, said diluent may be combined with the air and introduced through line 165 or it may be introduced through line 179.

In many cases, temperatures during 115 regeneration must be carefully controlled to avoid diminishing the absorptive or catalytic properties of the powdered or pulverized material. The apparatus illustrated in Fig. 2 permits careful regulation of the temperature obtained during regeneration. By locating the regenerating zone within a heat exchanger or waste heat boiler, by introducing the air at spaced points within the regenerating zone and by diluting the air with inert 120 125 130

diluent, such as recycled regenerating gases, a careful regulation of the temperature within the regenerating zone can be obtained. During regeneration it may be desirable to maintain the stream of regenerating gas and powdered material suspended therein under a substantial super-atmospheric pressure, such as from 2.20 atmospheres. By the use of pressure, a lower ignition temperature of the powdered material can be employed and the capacity of the regeneration zone increased.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:

1. A process for treating crude petroleum oil to obtain motor fuel of high antiknock value therefrom which comprises separating the oil into a plurality of fractions of different boiling ranges, vaporizing said fractions separately, suspending a solid pulverulent contact material in each of said separate fractions passing each of said suspensions of solid pulverulent contact material in an oil fraction through separate reaction zones and maintaining said suspensions in such reaction zones for such times and under such conditions as to convert the oil fractions into motor fuels of high antiknock value and separating the said motor fuels from the reaction products.

2. A process as claimed in claim 1, wherein the crude oil is separated into three fractions, namely a light fraction comprising principally hydrocarbons boiling within the gasoline range, an intermediate fraction comprising principally hydrocarbons boiling within the gas oil range and the third a heavy fraction comprising principally heavy residual hydrocarbons boiling above the gas oil range.

3. A process as claimed in claims 1 or 2, wherein the various fractions are vaporized and each fraction is introduced into a reaction zone in the form of a restricted stream of vapour and the pulverised contact material is introduced into the said stream of vapour before the entry into the reaction chamber, and the mixture is passed through the reaction chamber at such a velocity as to retain the pulverulent contact material in a state of suspension in the mixture during its passage through the reaction chamber.

4. A process as claimed in claim 3, wherein the reaction chamber is in the form of an elongated restricted passage way.

5. A process as claimed in claim 3, wherein the powdered contact material is

suspended in a current of an inert gas and this suspension of the contact material in inert gas is then introduced into the stream of vapour.

6. A process as claimed in claim 4, wherein the inert gas employed to form the suspension of the catalyst may be steam, nitrogen, or light hydrocarbon gases.

7. A process as claimed in any of the preceding claims, wherein the reaction products are separated from the contact material and are fractionated to obtain the motor fuel fractions therefrom.

8. A process as claimed in claim 7, wherein the bulk of the contact material is separated from the vaporous products in a dust separator for example a cyclone separator, whereupon the vapours are cooled and steam and heavier boiling oil fractions are condensed to form a condensate containing the last traces of catalyst which condensate is separated from the remaining oil vapours and the said oil vapours are fractionately condensed to obtain motor fuel fractions.

9. A process as claimed in claim 8, wherein the condensate is allowed to settle into an oil layer and an aqueous layer containing the separated catalyst, whereupon the oil layer is separated off and combined with the uncondensed reaction products and mixture thus obtained is fractionated to obtain the constituents boiling within the motor fuel range.

10. A process as claimed in claims 2 to 9, wherein the light fraction comprises gasoline oils of low anti-knock value and is treated with a reforming catalyst capable of improving materially the anti-knock properties of the motor fuel.

11. A process as claimed in claim 10, wherein the reforming catalyst is selected from the group comprising active, or activated clays, mixed oxides of silica, alumina, bauxite or mixed oxides of elements of the third and sixth groups of the periodic system.

12. A process as claimed in claims 2 to 10, wherein the light naphtha fraction is treated with a combined reforming and condensing catalyst.

13. A process as claimed in claim 12, wherein the catalyst employed is selected from the group comprising activated clays aluminium chloride or complex salts of aluminium chloride employed alone or on a suitable carrier.

14. A process as claimed in claims 10 to 13 inclusive, wherein the reforming reaction is carried out at a temperature between 400—1000° F.

15. A process as claimed in claims 2 to 9, wherein the intermediate gas oil fraction is treated with a cracking catalyst.

16. A process as claimed in claim 15, wherein the cracking catalyst employed is selected from the group comprising active or activated clays and synthetic gels, preferably of silica or alumina. to 3 parts by weight of the solid material per part by weight of oil.
17. A process as claimed in claims 15 or 18 wherein the cracking reaction is carried out at a temperature between 800 and 1000° F., preferably between 875 and 925° F. and at a pressure between 1 and 20 atmospheres. 23. A process as claimed in any of the preceding claims wherein the solid material is employed in the form of a 50 fine powder between 200—400 mesh.
18. A process as claimed in claims 2 to 9 wherein the heavy residual oil fraction is treated with a contact material adapted to form a carrier for coke formed during the reaction and mixture is maintained in the reaction zone for such a time and under such conditions as to convert the heavy residual oil into the hydrocarbons of lower boiling point and/or to reduce the viscosity of the said residual oils. 24. A process as claimed in any of the preceding claims, wherein the reaction products are fractionated to separate a normally gaseous fraction and a motor fuel fraction therefrom and the said normally gaseous fraction is returned to the reaction chamber. 55
19. A process as claimed in claim 18, wherein the contact mass employed is selected from the group comprising active cracking catalysts or inactive cracking catalysts, inert materials, such as pumice, kieselguhr, spent clay and other solid absorbent materials. 25. A process as claimed in claim 22 wherein the normally gaseous fraction from the reaction products recycled to the reaction zone contains substantial quantities of hydrogen. 60
20. A process as claimed in claims 17 and 19, wherein the reaction products of the treatment of the heavy residual oils boiling within the gas oil range are further treated by the process as claimed in claims 15 to 17. 26. A process as claimed in claims 24 or 25, wherein hydrogen or gases containing substantial amounts of hydrogen are added to the gases being recycled. 65
21. A process as claimed in claims 2 to 9, wherein the reaction products from the treatment of the heavy residual oil boiling within the gas oil range are combined with the intermediate gas oil fraction and the mixture is treated by the process as claimed in claims 15 to 17. 27. A process as claimed in any of the preceding claims, wherein prior to their introduction into the reaction chambers 70 the vaporised fractions are mixed with a gaseous fraction containing substantial quantities of hydrogen. 70
22. A process as claimed in any of the preceding claims, wherein the solid material used for treating the oil fraction is employed in the proportion of from 0.5 to 3 parts by weight of the solid material per part by weight of oil. 28. A process as claimed in any of the preceding claims wherein after separation from the reaction products the contact materials are subjected to a regeneration treatment in the presence of oxidizing gases to remove carbonaceous deposits contained thereon and the regenerated 75 contact materials are returned to the reaction zone. 80
29. The process for the treatment of crude petroleum oils substantially as hereinbefore described. 85

Dated this 19th day of May, 1941.

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FIG.-1

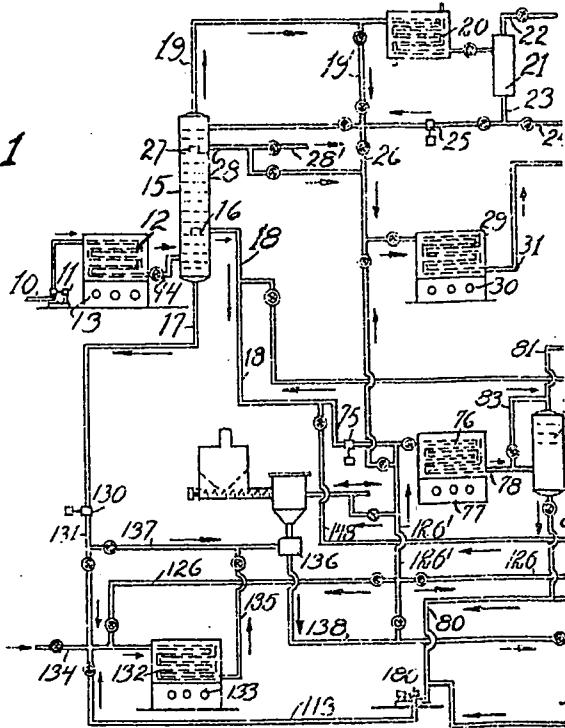
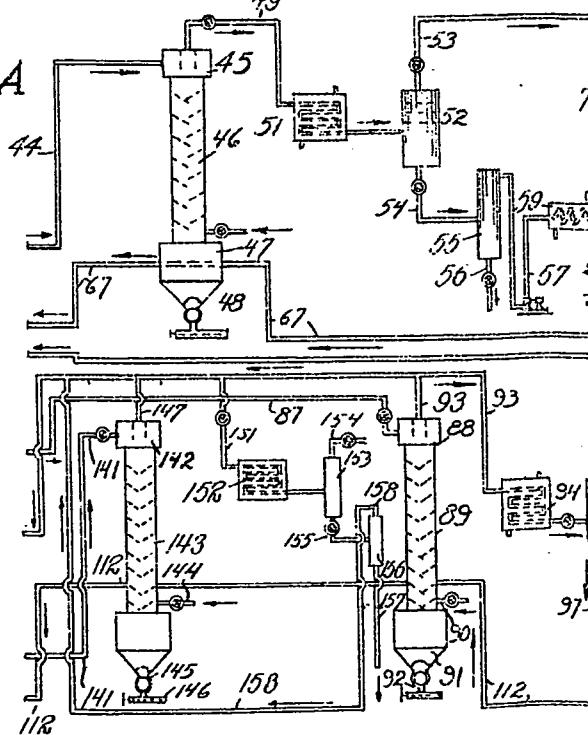
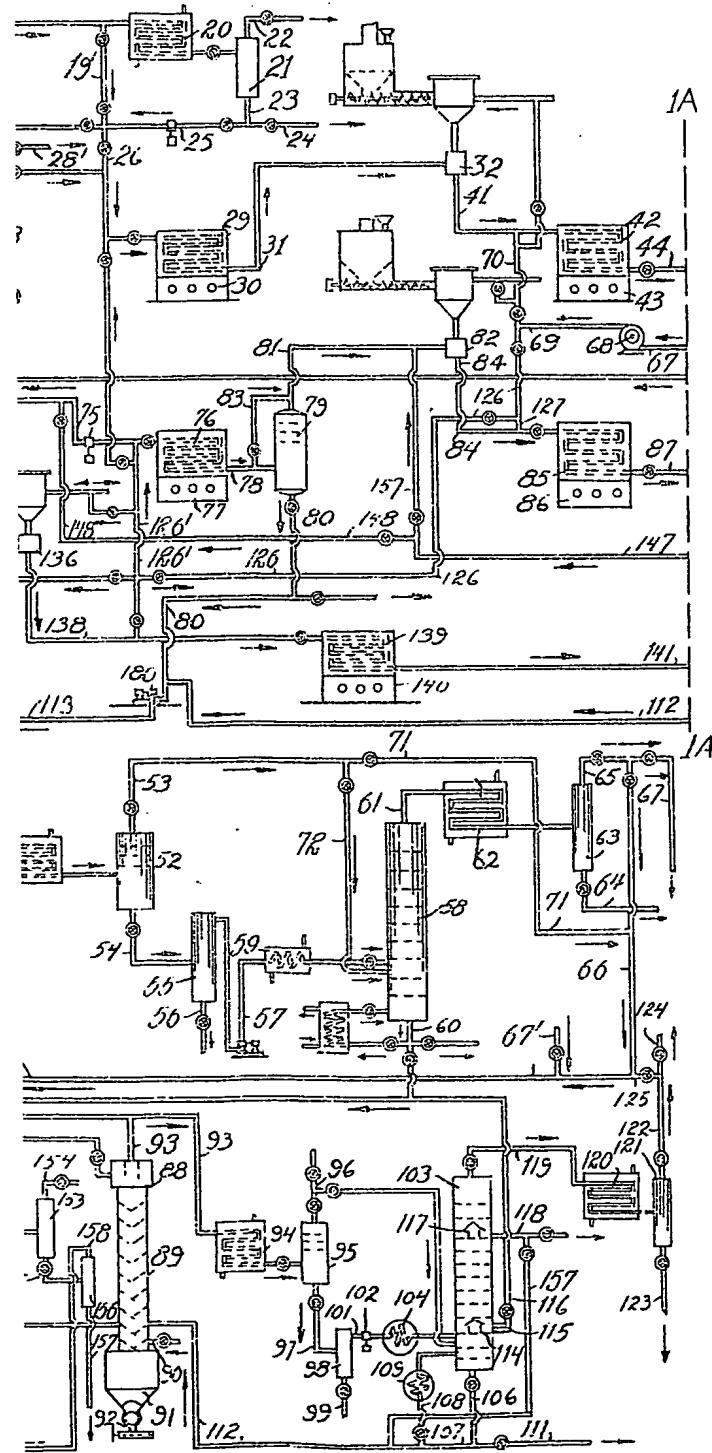


FIG.-1A





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FIG.-1

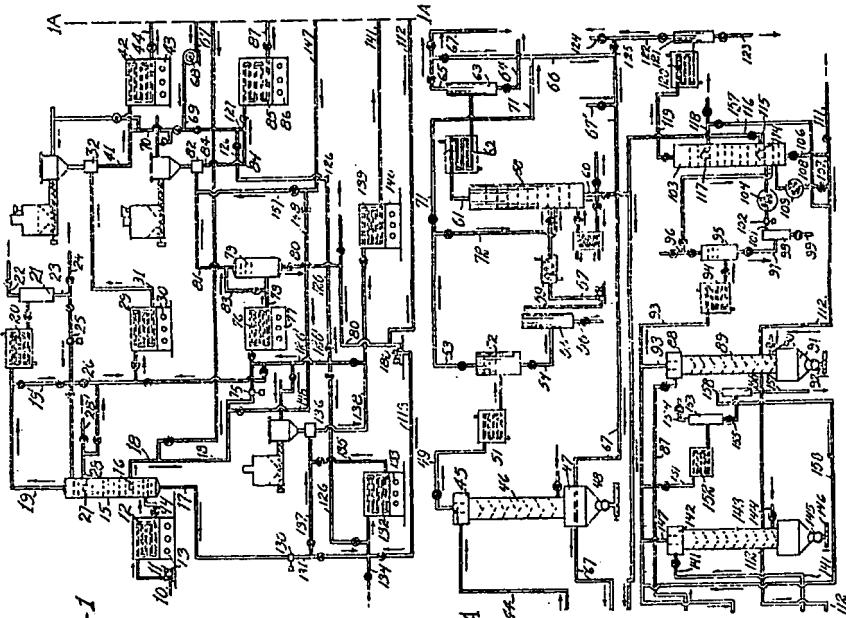


FIG.-1A

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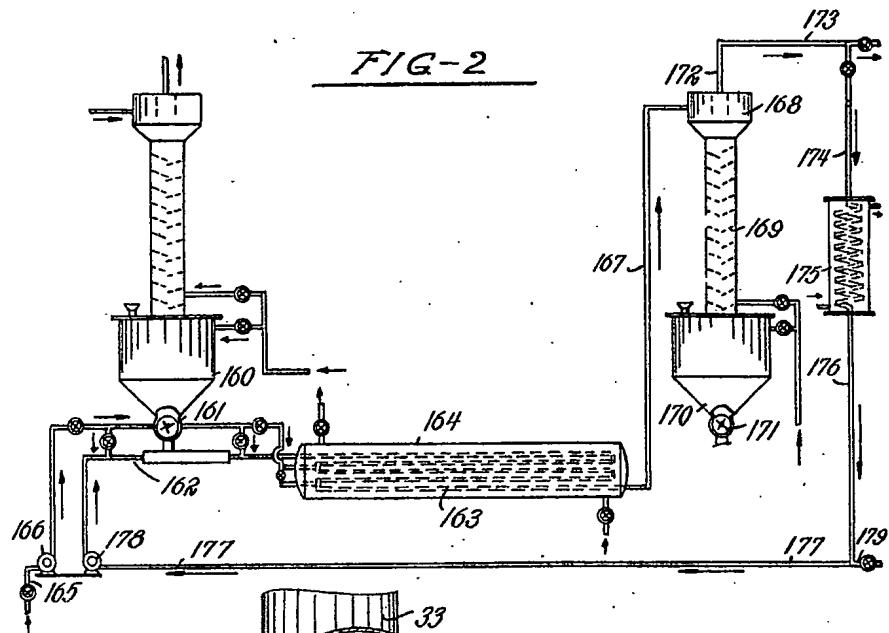


FIG.-3

